

High Ionic Conductivity and Transfer Number of Composite Solid Electrolyte for Advanced Lithium Battery by Synergetic Effect of Halloysite Nanotube and High-entropy Zeolitic Imidazolate Frameworks

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Electronic Supplementary Information

Abstract Composite solid-state electrolytes (CSEs) with excellent flexibility and high safety hold great potential for high performance lithium batteries. However, its low room temperature ionic conductivity and transfer number have plagued its practical application. In this work, local Li diffusion was tailored by the synergetic effect of halloysite nanotubes (HNTs) and high-entropy ZIF in a polyvinylidene fluoride/LITFSI/Li_{6.85}La_{2.95}Yb_{0.05}Zr_{1.85}Ta_{0.15}O₁₂ matrix. The anchoring of TFSI⁻ anions by the rich open metal sites in HE-ZIF and the inner positively wall in HNT, combined with the continuous diffusion pathway of Li⁺ built by the negatively surface of HNT, distinctly enhances the ionic conductivity and transfer number of the electrolyte. A high ionic conductivity ($1.06 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C) and high Li⁺ transference number (0.86) were achieved in PLLH-HE. The lithium symmetric battery (Li//PLLH-HE//Li) exhibited excellent interfacial compatibility and a high critical current density (CCD, 2.38 mA·cm⁻²). A lithium metal battery assembled with LiFePO₄ (LFP) cathodes exhibited a high discharge specific capacity of 141 mAh·g⁻¹ after 400 cycles at 0.5 C, while the cell assembled with LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) also delivered a high discharge specific capacity of 140.1 mAh·g⁻¹ at 1 C after 600 cycles. This work reveals the critical role of local Li diffusion and provides a general method for enhancing the electrochemical properties of CSEs for solid state batteries.

Keywords Composite solid-state electrolytes; Lithium-ion conductivity; Transfer number; Halloysite nanotubes; High-entropy ZIF; Synergetic effect

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INTRODUCTION

Lithium-ion batteries (LIBs) are the most widely used energy storage devices in electric vehicles and portable electronic devices, which are plagued with significant safety risks owing to the flammable and leak-prone properties of the organic liquid electrolytes they utilize.^[1–5] To tackle these problems, solid-state electrolytes, including organic solid polymer electrolytes (SPEs), inorganic solid-state electrolytes (SSEs), and composite solid-state electrolytes (CSEs), have emerged as a transformative solution.^[6–9] Among them, CSEs are a multiphase electrolyte system formed by physical blending or chemical reaction of organic polymers (poly(vinylidene fluoride) (PVDF),^[10,11] poly(ethylene oxide) (PEO),^[12] poly(methyl methacrylate) (PMMA),^[13] polyacry-

lonitrile (PAN)^[14] and inorganic/functional fillers (inorganic fillers: Li₇La₃Zr₂O₁₂ (LLZO) and its derivatives,^[15–21] Li_{0.35}La_{0.55}TiO₃ (LLTO),^[22] Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP),^[23] Li₁₀GeP₂S₁₂ (LGPS),^[24] SiO₂,^[25] and Al₂O₃,^[26] functional fillers: halloysite nanotubes (HNTs),^[27–31] metal-organic frameworks (MOFs)^[32]). Their core characteristic stems from the multi-phase synergistic effect brought by “compositing”, retaining the flexibility, processability, and interfacial adaptability of polymers while integrating the high ionic conductivity (σ), mechanical robustness, and chemical stability of inorganic phases.

Despite significant progress in current research on CSEs, their performance remains constrained by the limited regulation of single or binary fillers, which fails to harness the full potential of multi-component synergy. For instance, incorporating single filler into polymers can effectively enhance the σ , mechanical properties, and interfacial compatibility of CSEs, but the σ hardly exceeds $10^{-3} \text{ S} \cdot \text{cm}^{-1}$, and the Li⁺ transference number (t_{Li^+}) remains in the range of

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0.3–0.6.^[20,21,25–28,32,33] As active fillers for CSE, LLZO and its derivatives have a lower energy barrier for Li⁺ migration and a higher σ (up to 10^{-3} S·cm⁻¹ at room temperature (RT)).^[34,35] Introducing LLZO and its derivatives into the polymer matrix effectively improves the σ of CSEs by inhibiting polymer crystallization and constructing special ionic transport channels at the filler/polymer interface. The CSE consisting of Li_{6.5}La₃Zr_{1.5}Ta_{0.1}Nb_{0.4}O₁₂ (LLZTNO) and PVDF exhibited a high RT σ (1.05×10^{-4} S·cm⁻¹) and t_{Li^+} (0.66).^[18] Cheng *et al.* prepared the CSE by compounding Li_{6.28}La₃Zr₂Al_{0.24}O₁₂ (LLZAO) with PVDF, which also achieved an σ of 1.2×10^{-4} S·cm⁻¹ and favorable interfacial stability with lithium metal.^[19] Zeolitic imidazolate frameworks (ZIFs), as an important subclass of MOFs, have a high specific surface area, porous structure, and exposed metal sites.^[36,37–40] They can promote the migration of Li⁺ by selectively adsorbing large-sized anions.^[36,41–43] Benefiting from the above excellent properties, ZIF was mixed with polymers to optimize the ionic transport performance of CSEs. Jiang *et al.* fabricated a PVDF/ZIF-8 based CSE via the casting method, its RT σ was 1.5×10^{-4} S·cm⁻¹ and the t_{Li^+} reached as high as 0.83, which indicated that the ZIF-8 has built stable channels for Li⁺ transition.^[41] Du *et al.* prepared a PVDF/LiTFSI/ZIF-8 electrolyte using the same method; its σ (0.86×10^{-4} S·cm⁻¹) was 4.3 times of that for PVDF/LiTFSI electrolyte.^[42] Obviously, the incorporation of a single filler into the polymer matrix could effectively improve the σ of CSEs, yet its RT σ was still less than 10^{-3} S·cm⁻¹.

Nevertheless, the incorporation of dual fillers can synergistically enhance the electrochemical performance of the CSEs. In Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP)/LLZO/LiTFSI@UiO-66(F) electrolyte, the t_{Li^+} (0.51) and σ (4.9×10^{-4} S·cm⁻¹) were both approximately twice those of the electrolyte without UiO-66 added.^[44] Yang *et al.* synthesized a high-performance CSE (PLZ) using LLZO@ZIF-67 as the filler and PEO as the matrix. Compared with the single-filler CSEs (PL and PZ), PLZ exhibited an σ nearly one order of magnitude higher, and the t_{Li^+} was enhanced by 1.3 of 2.2 times.^[33]

In contrast to the general ZIF with only one type of metal ion, the high-entropy ZIF incorporates a minimum of five metallic elements at near-equimolar ratios. The significant lattice distortion induced by multiple ions with different radii facilitates the formation of defects, thereby exposing different open metal sites.^[45,46] Recently, our group first synthesized the high-entropy ZIF by mechanical ball milling and incorporated HE-ZIF into a PVDF matrix via the casting method. Through the synergetic effect between LLYZTO and HE-ZIF, the t_{Li^+} and σ of the as-prepared CSE have been sharply enhanced to 0.84 and 7.76×10^{-4} S·cm⁻¹, respectively.^[36] Although LLZO and HE-ZIFs particles can form local fast ion diffusion pathways in polymers, random dispersion of these particles usually forms discontinuous ion transport pathways, which indicates that inevitable and slow Li⁺ diffusion through the PVDF/LiTFSI matrix, suppressing the further enhancement of the overall t_{Li^+} and σ .

One-dimensional (1D) materials can bridge the discrete particles, construct a continuous conduction network, and effectively facilitate the ion diffusion in CSEs. Halloysite nanotube (HNT) is a low-cost natural 1D tube-like aluminosilicates. Its high aspect ratio, rigidity, and heat resistance also

improved the mechanical properties and thermal stability of CSEs.^[27–31] The high aspect ratio indicates that it can build local continuous pathway for Li⁺ diffusion. More interestingly, it possesses multilayered walls with negatively charged outer silica and positively charged inner alumina. This indicates that there should be some special electronic separation of the isolated Li⁺ and TFSI⁻ ions in the polymer matrix. Leveraging the unique structure of HNTs, a suitable amount of LiPF₆ liquid (1 mol·L⁻¹) was immersed into the porous electrolyte film of PTFE binding ZIF-8 and HNTs, which resulted in an excellent single ion electrolyte with record-high σ (7.74×10^{-3} S·cm⁻¹) and t_{Li^+} (0.84).^[47] Logically, by integrating the anchoring effect for the anions of high-entropy ZIF and HNT with the bridge effect of the 1D negatively charged outer layer of HNT, more effective Li diffusion could be anticipated in the CSE.

In this study, 1D HNTs were incorporated into the PVDF/LLYZTO/HE-ZIF matrix, and the effect of HNT and the synergetic effect of HNT and HE-ZIF on the structure and electrochemical properties were investigated. The as-prepared PLLH-HE exhibited remarkable σ (1.06×10^{-3} S·cm⁻¹), t_{Li^+} (0.86), and low activation energy (0.13 eV), as well as excellent mechanical properties (14.63 MPa) and thermal stability. The Li symmetric cell showed a high CCD of 2.38 mA·cm⁻². The assembled LFP//PLLH-HE//Li and NCM811//PLLH-HE//Li cells delivered discharge specific capacities of 141 mAh·g⁻¹ and 140.1 mAh·g⁻¹ after 400 and 600 cycles at 0.5 and 1 C, respectively. This work provides a general and effective method to enhance the σ and t_{Li^+} by regulating the local Li⁺ diffusion.

EXPERIMENTAL

The experimental details are included in the electronic supplementary information, ESI.

RESULTS AND DISCUSSION

Fig. 1(a) presents the process of PLLH-HE by the casting method. To illustrate the idea of the PLLH-HE CSE design, Fig. 1(b) presents the transport of Li⁺ and TFSI⁻ in PLLH-HE. The left-side structural schematic shows the distribution of each component in the CSE; the local enlarged frame elucidates the specific transport mechanisms of Li⁺ and TFSI⁻ in HE-ZIF and HNTs. HNT has a hollow tube-like structure with positive inner and negative outer surfaces, confining TFSI⁻ inside it to some extent, while its negatively charged outer surface allows Li⁺ to migrate rapidly.^[27,28] On the other hand, the porous crystal structure of HE-ZIF provided abundant internal transport channels for the rapid migration of Li⁺, and its sub-nanoscale channels could hinder the migration of larger-sized TFSI⁻ through the steric hindrance effect.^[36,41] LLYZTO with high Li⁺ conductivity promoted lithium salt dissociation, increased Li⁺ concentration, and reduced crystallinity of PVDF, providing a highly conductive interface and simultaneously inhibiting interfacial side reactions and lithium dendrites. Figs. 1(c) and 1(d) further compare the different Li⁺ transport pathway in CSEs: the ion transport channels individually formed by LLYZTO and HE-ZIF were in a discontinuous and isolated state due to their content; after the introduction of HNTs, they could construct many local continuous rapid Li⁺ conduction network between different filler particles by virtue of the negatively charge surface, which avoids the slow

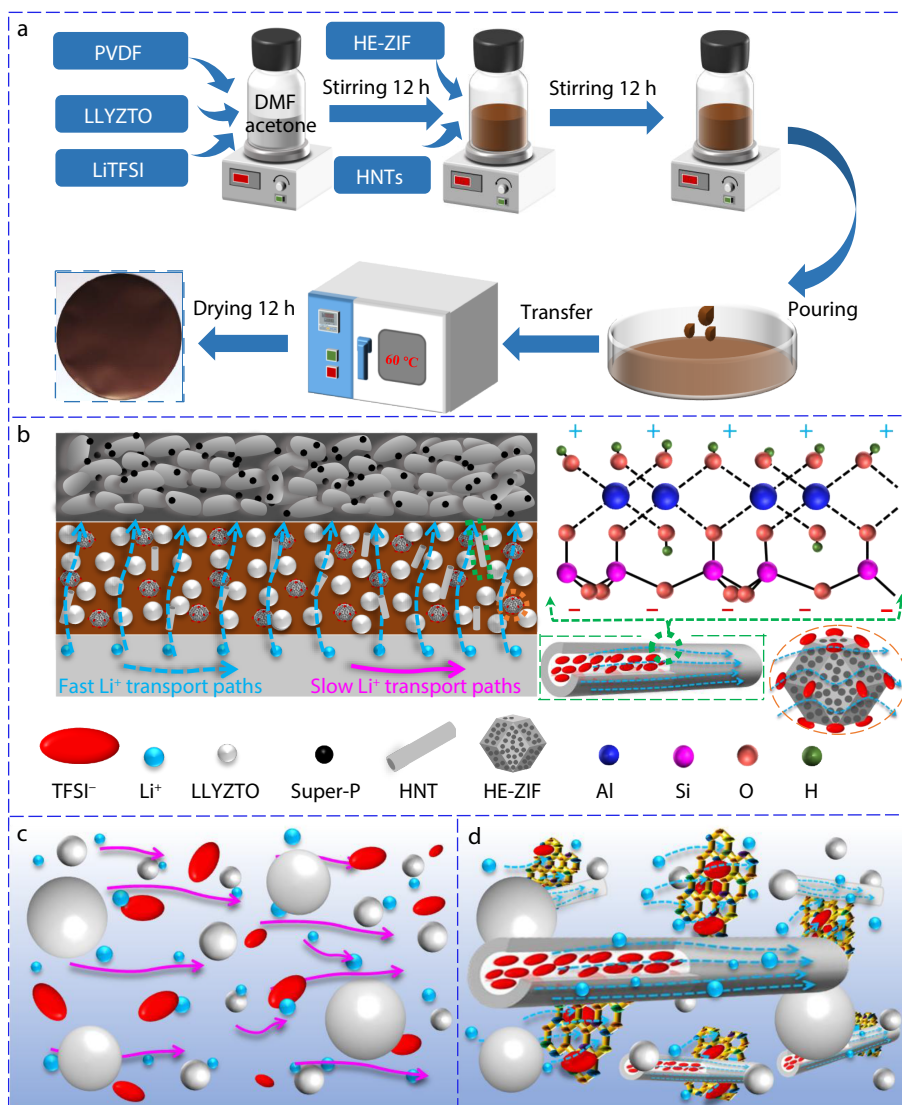


Fig. 1 (a) Schematic of PLLH-HE synthesis; (b) Schematic of HE-ZIF and HNTs functions in CSE; (c, d) Li⁺ transport modes in CSE.

diffusion through PVDF/LiTFSI matrix. On the other hand, HE-ZIF selectively suppresses the motion of the large TFSI⁻ while allow the small Li⁺ to diffuse rapidly. All components, through their synergistic effect, constructed an efficient pathway for Li⁺ transport, beneficial for enhancement of transfer number of Li⁺.

Fig. 2(a) shows the X-ray diffraction (XRD) patterns of PLL, PLL-HE, PLL-HNTs and PLLH-HE. The main characteristic diffraction peaks of the four CSEs are consistent with those of the highly conductive cubic phase LLYZTO (JCPDF-45-0109). This indicated that LLYZTO was successfully introduced into the PVDF matrix.^[17] After the addition of LLYZTO, the crystallinity of the polymer was reduced.^[36] The weak diffraction peaks at approximately 12.7° and 17.9° in PLL-HE and PLLH-HE correspond to the (112) and (222) crystal planes of HE-ZIF, respectively. For CSEs containing HNTs (PLL-HNTs, PLLH-HE), the weak diffraction peak appearing at approximately 12.2° corresponds to the (001) crystal plane of HNTs. The individual XRD patterns of LLYZTO, HE-ZIF, and HNTs are shown in Figs. S1–S3 (in the electronic supplementary information, ESI).

For PVDF-based composites, the polar β -phase, which has a

higher dielectric coefficient than α -phase, facilitates Li⁺ diffusion.^[2,10] Fourier transform infrared spectroscopy (FTIR) spectra of PLL-HNTs and PLLH-HE showed that the weak absorption peaks at 613 and 761 cm⁻¹ were associated with α -phase PVDF, while the strong characteristic absorption peaks at 836, 877, 1173, 1230 and 1392 cm⁻¹ corresponded to β -phase PVDF (Fig. 2b and Fig. S4a in ESI).^[48] The characteristic C=C peak at 1662 cm⁻¹ was related to the dehydrofluorination reaction.^[49] The β -phase contents of PLL-HNTs and PLLH-HE calculated from the Lambert-Beer law (Eq. S1 in ESI), were 60.14% and 62.06%, respectively (Fig. 2c). Compared with the previous research,^[36] the β -phase contents of the two samples increased, which indicating enhanced Li⁺ transport kinetics. Raman spectroscopy was used to examine the influence of the synergistic effect on lithium salt dissociation. As shown in Fig. S4(b) (in ESI), the proportions of solvent-separated ion pairs (SSIP), contact ion pairs (CIP) and aggregates (AGG) in PLL were 48.34%, 15.18%, and 36.48%, respectively. Theoretically, a high proportion of SSIPs and a low proportion of AGG meant more efficient dissociation of lithium salt, which was

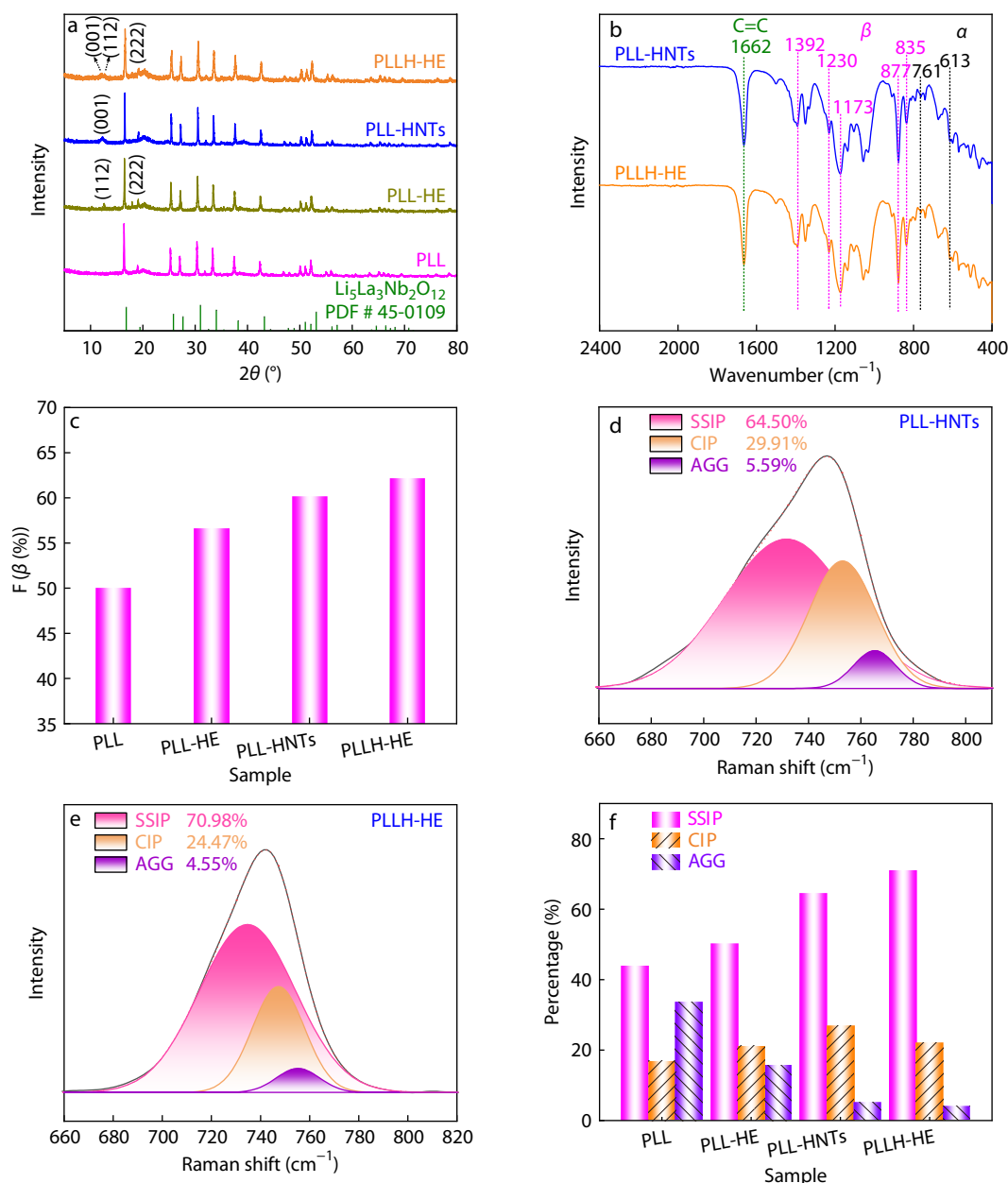


Fig. 2 (a) XRD patterns of PLL, PLL-HE, PLL-HNTs and PLLH-HE; (b) FTIR spectra of PLL-HNTs and PLLH-HE; (c) β -phase content of PVDF; (d, e) Local Raman spectra of PLL-HNTs and PLLH-HE; (f) The contents of solvent-separated ion pair (SSIP), contact ion pairs (CIP), and aggregates (AGG) in PLL, PLL-HE, PLL-HNTs, and PLLH-HE.

beneficial to the rapid conduction of Li^+ .^[36] After the introduction of HE-ZIF or HNTs alone, the proportion of SSIPs increased significantly, whereas the proportion of AGGs decreased obviously, as shown in Fig. S4(c) (in ESI) and Fig. 2(d). As shown in Figs. 2(e) and 2(f), compared with the other three CSEs, PLLH-HE exhibited the highest SSIP proportion (70.98%) and the lowest AGG proportion (4.55%). This indicates a synergistic effect between the HE-ZIF with multi-metallic active sites and HNT with an electrically negative surface,^[29,50] thereby jointly facilitating the dissociation of lithium salts. Specifically, the positive internal and negative external charge characteristics of HNT could achieve the efficient dissociation of lithium salts via the spatial selective electrostatic separation

effect, and then increased the concentration of free Li^+ . NH_3 -TPD analysis results show that HE-ZIF exhibits a higher NH_3 desorption peak intensity than ZIF-8 with a single metal ion, confirming the high concentration of the exposed unsaturated open metal ion sites (Lewis acidic) (Fig. S5 in ESI).^[51] More free SSIPs prompt the diffusion of Li^+ . Moreover, the increased ratio of CIPs and the decreased ratio of AGG in PLL-HE, PLL-HNTs, and PLLH-HE not only enhanced the ion transport performance but also suppressed side reactions at the electrode-electrolyte interface.^[36] Specifically, the increased CIPs ratio and decreased AGG ratio effectively reduced anion enrichment and aggregation at the electrode interface, alleviated concentration polarization and suppressed electrolyte

decomposition. Meanwhile, they promoted the formation of a compact and stable interfacial layer, thereby significantly reducing interfacial side reactions.

Figs. 3(a)–3(f) and Fig. S6 (in ESI) presented the surface and cross-sectional scanning electron microscopy (SEM) images of the CSEs. As seen in Figs. 3(a), 3(d) and Figs. S6(a), S6(d) (in ESI), the surfaces of PLL, PL-HE, PLL-HNTs, and PLLH-HE were smooth and dense without obvious visible pores, which indicating that LLYZTO, HNTs, and HE-ZIF were uniformly distributed in the PVDF matrix. The cross-sectional images and their local magnified images showed that the four CSEs were compact and continuous, and no agglomeration of LLYZTO, HNTs and HE-ZIF was observed (Figs. 3b, 3c, 3e, 3f and Figs. S6b, S6c, S6e, S6f in ESI). The SEM images of LLYZTO (average particle size: 0.32 μm), HNTs (average length: 1.18 μm), and HE-ZIF (average particle size: 78.48 nm) powders are shown in Fig. S7 (in ESI). Notably, tube-like HNTs (indicated by arrows) with diameter of 140 nm are observed in Figs. 3(c) and 3(f), and the partial pull-out of some nanotubes contributed to the enhancement of the CSE's mechanical properties. Energy-dispersive spectrometry (EDS) element mapping showed the overall distribution of various elements in PLLH-HE (La, Zr, Ta, Al, Si, Mg, Zn, Co, Ni, Cu, etc.) and further confirmed the uniform dispersion of the above three fillers (Fig. S8 in ESI). To further elucidate the nanoscale surface characteristics and ion

transport behavior, Kelvin probe force microscopy (KPFM) measurements were conducted. As illustrated in Figs. 3(g)–3(i), the surface of PLLH-HE exhibited uniform micro-nanoscale undulations, with an average surface roughness of only 25.04 nm, which confirmed its flat and smooth surface. In addition, the surface potential distribution indicated that the surface potentials of LLYZTO particles and HNTs tubes (indicated by red ellipses) were higher than that of the polymer matrix, which demonstrated the enrichment of Li^+ on their surfaces and provided direct evidence that HNTs acted as continuous ion transport channels between LLYZTO particles and mediated the rapid migration of Li^+ along the surface of the HNTs.

The excellent mechanical properties of CSEs are crucial for improving the cycling stability and safety of Li-metal batteries (LMBs).^[52] Optical images of the PLLH-HE revealed its smooth and dense morphology, excellent flexibility, and foldability, ensuring good compatibility with the cathode/anode (Fig. S9 in ESI). As shown in Fig. 4(a), the maximum mechanical strength and elongation at break of the PLL were 9.30 MPa and 176.64%, respectively. After the introduction of HE-ZIF, the strength was enhanced by approximately 23.65% owing to the blocking of the segment movement of PVDF. Compared with HE-ZIF, the strength of the composition with HNT reached about 13 MPa. More importantly, significant im-

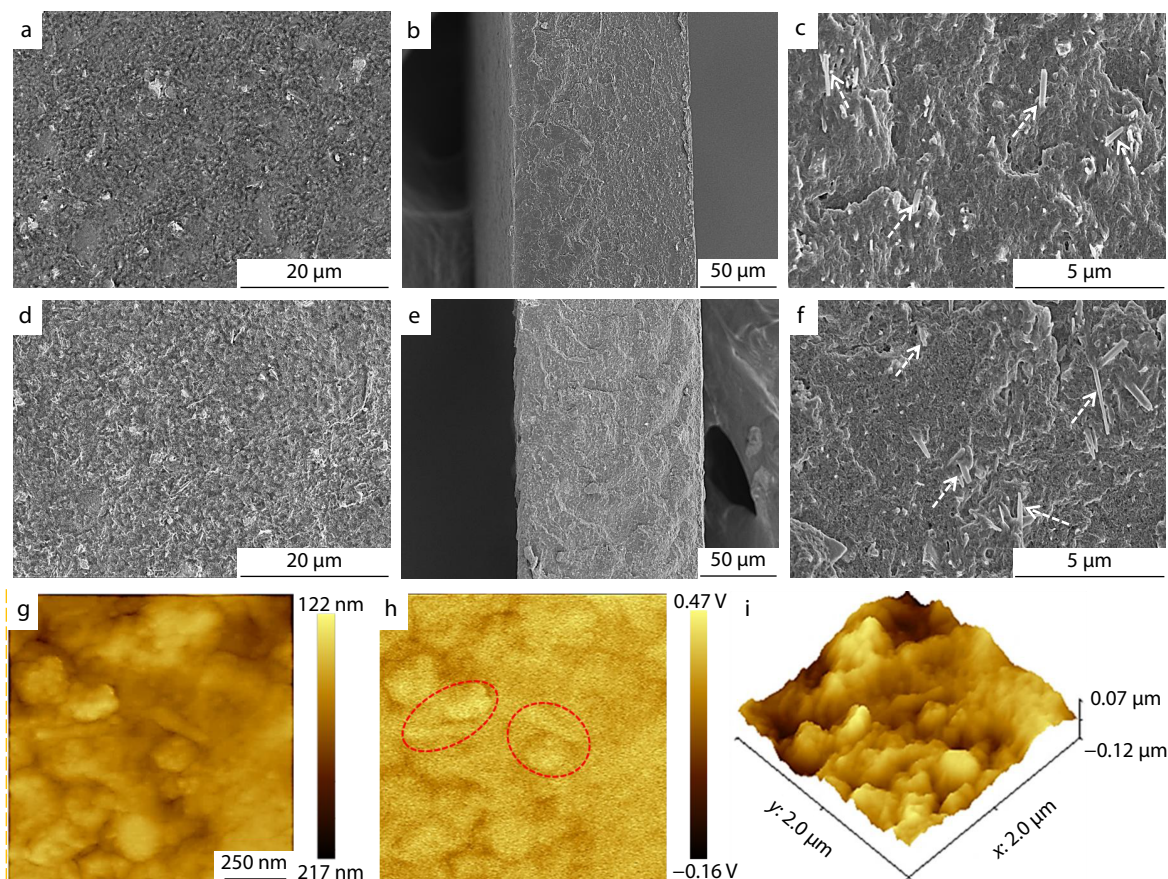


Fig. 3 (a–c) Surface, cross-sectional and magnified cross-sectional SEM images of PLL-HNTs; (d–f) Corresponding images of PLLH-HE (Samples were prepared by liquid nitrogen quenching; White arrow refers to the needle-like HNTs; Red ellipses indicate the surface potentials of LLYZTO and HNTs); (g–i) AFM images of PLLH-HE.

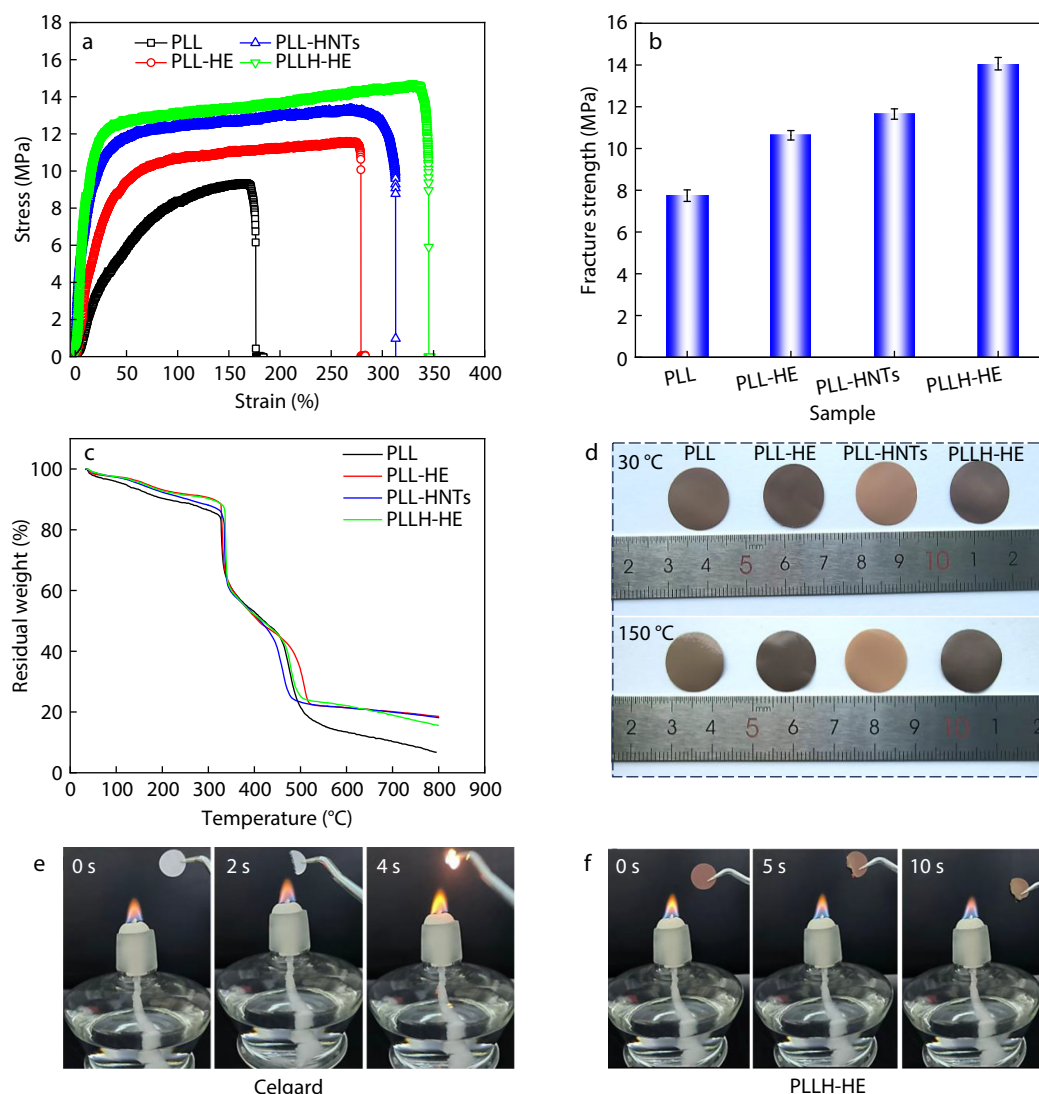


Fig. 4 (a) Stress-strain curves of PLL, PL-HE, PLL-HNTs, and PLLH-HE; (b) Corresponding fracture strength; (c) TGA curves of PLL, PL-HE, PLL-HNTs, and PLLH-HE; (d) Optical photographs of PLL, PL-HE, PLL-HNTs, and PLLH-HE after high-temperature treatment at 150 °C for 1 h; (e, f) Combustion test of Celgard separator and PLLH-HE.

improvements in these two properties were obtained with the simultaneous addition of HE-ZIF and HNTs, where PLLH-HE showed the best comprehensive performance (mechanical strength: 14.63 MPa, elongation at break: 345.38%), which surpassed those of other reported PVDF/LLZO-based CSEs.^[17,48]

This indicates that the synergetic effect between HE-ZIF and HNTs could effectively enhance the mechanical properties of CSEs. HE-ZIF with organic ligands is preferred to be uniformly dispersed in the polymer, which not only improves the density of the CSE but also efficiently suppresses the relative slippage of the polymer chains under external stress;^[36,41,53] HNTs, on the other hand, homogenizes the stress distribution and improves the stress transfer in the PVDF.^[28,54] Additionally, the uniform dispersion of HE-ZIF nanoparticles and tube-like HNTs in the PVDF matrix facilitated energy dissipation during deformation and hindered crack propagation, leading to the simultaneous improvement in both mechanical strength and

elongation at break. The enhanced mechanical properties reduced the risk of being pierced by lithium dendrites (Fig. 4b).^[29,52] To examine the thermal stability of the CSEs, thermogravimetric analysis (TGA) was performed over a temperature range from room temperature to 800 °C (Fig. 4c). In the low temperature region (<320 °C), the composite electrolytes exhibited a weight loss of approximately 10%–14% due to the volatilization of residual moisture and the organic solvent (*N,N*-dimethylformamide (DMF)). It is difficult to completely remove DMF during the synthesis process because of its strong interaction with lithium ions.^[49] From 320 °C to 460 °C, PLL, PLL-HE, PLL-HNTs, and PLLH-HE all exhibited significant thermal weight loss as result of the decomposition of the PVDF and the LiTFSI.^[16] Notably, compared with PLL (initial decomposition temperature: 327 °C), the decomposition temperatures of PLL-HE (329 °C), PLL-HNTs (334 °C), and PLLH-HE (337 °C) were slightly higher, which indicated that the introduction of both HE-ZIF and HNTs fillers was beneficial for the

thermal stability of the CSEs. Specifically, the uniformly dispersed HE-ZIF and HNTs acted as physical barriers in the polymer matrix, which effectively hindered the transfer of heat and slowed down the thermal degradation process. Meanwhile, they formed a reinforced skeleton and restricted the thermal motion of PVDF molecular chains.^[28] The weight loss observed from 460 °C to 520 °C originates from the oxidation of residual carbonaceous materials.^[55,56] The TGA results indicated that PLLH-HE possesses the optimal thermal stability and higher safety. To further confirm the thermal stability of the CSEs, the four samples with diameters of 16 mm were heated at 150 °C for 1 h (Fig. 4d). There were no obvious

changes in the color or morphology of all samples after heat treatment. However, PLLH-HE showed the smallest changes in diameter, indicating its higher stability. The homogeneous distribution of HNTs in the polymer matrix formed a physical support network, effectively inhibiting the molecular chain creep and slippage of the matrix when heated, and thus reducing macroscopic shrinkage, which can effectively inhibit interfacial delamination between the electrolyte and electrodes, and improve the battery cycling stability. Furthermore, the combustion tests demonstrated that PLLH-HE possessed obvious flame retardancy, with no smoke or flame observed after 10 s, whereas the commercial Celgard separator

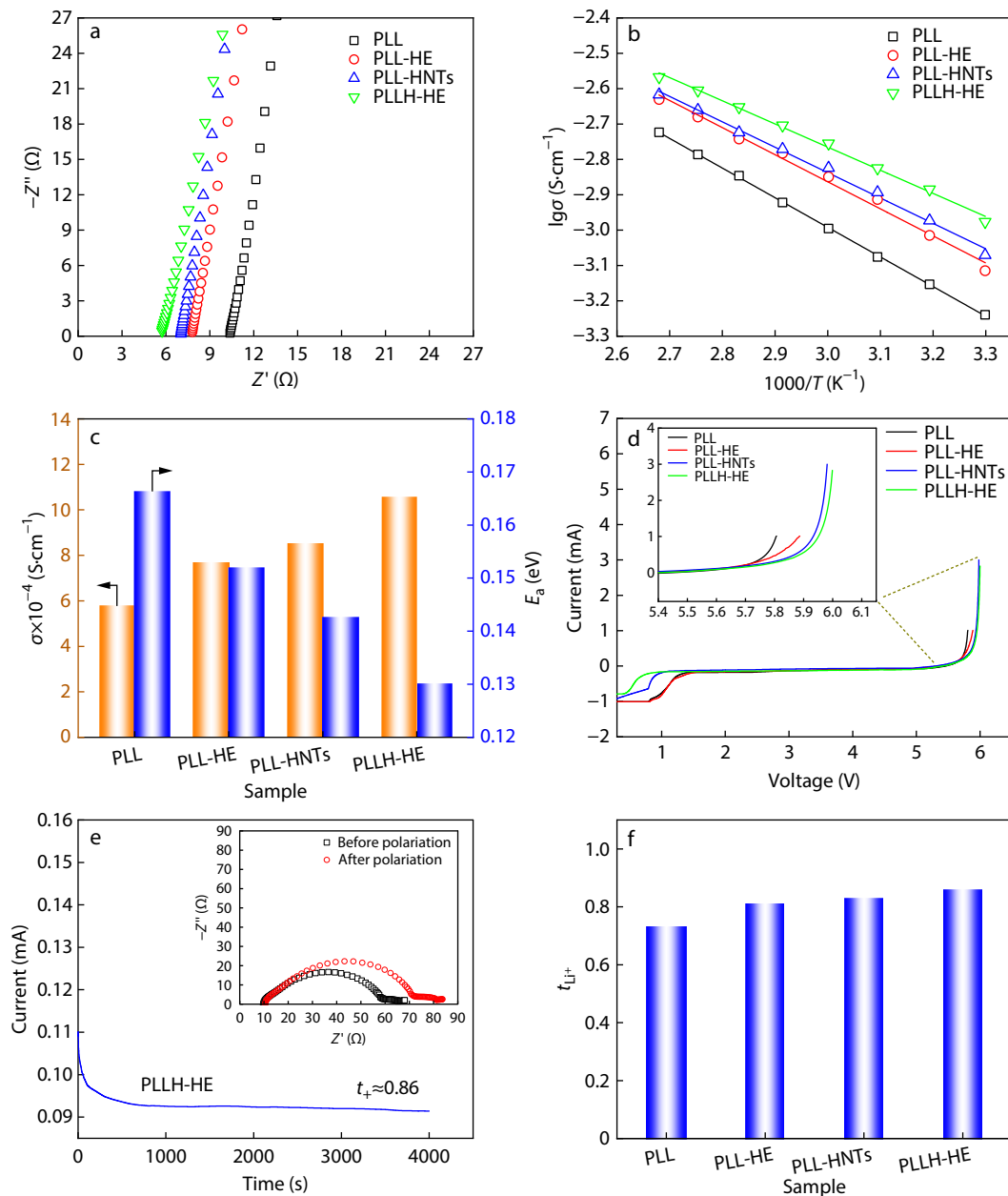


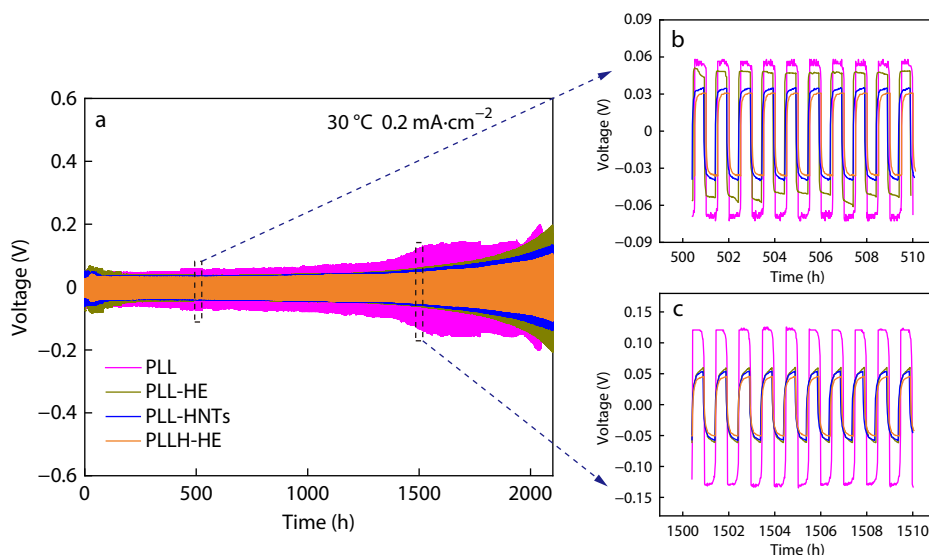
Fig. 5 (a) Nyquist plots of PLL, PLL-HE, PLL-HNTs and PLLH-HE at 30 °C; (b) Corresponding Arrhenius plots; (c) Ionic conductivities and activation energy; (d) LSV; (e) Curve of PLL-HE (The inset shows the Nyquist impedance spectra of the cell before and after polarization); (f) Ionic transference numbers for different CSE.

shrank rapidly and ignited to burn (Figs. 4e and 4f). In addition, the contact angle test results were in descending order: PLL (46.5°) > PLL-HE (41.5°) > PLL-HNTs (35.0°) > PLLH-HE (29.5°), indicating that the incorporation of HNTs and HE-ZIF significantly enhanced the wettability of the CSE, thereby optimizing the electrolyte/electrode interfacial compatibility and improving the long-term cycling stability of the batteries (Fig. S10 in ESI).^[57]

To evaluate the σ of the CSEs, electrochemical impedance spectroscopy (EIS) was tested on stainless steel symmetric batteries (SS//CSEs//SS). Fig. 5(a) shows the Nyquist plots of the different CSEs at 30 °C. The PLLH-HE showed lower impedance (5.68 Ω) than those of PLL-HNTs (7.02 Ω), PLL-HE (7.78 Ω) and PLL (10.36 Ω). PLL-HE (7.68×10^{-4} S·cm⁻¹) exhibited higher σ than PLL (5.76×10^{-4} S·cm⁻¹) due to the abundant micropores of HE-ZIF that could spatially restrict the larger TFSI⁻ and facilitate the transport of Li⁺.^[36,41–43] After the introduction of HNTs into the PLL, the σ of PLL-HNTs was significantly improved (8.5×10^{-4} S·cm⁻¹), which was ascribed to the hollow tube-like structure of HNTs allowed TFSI⁻ to be firmly anchored on the positively charged inner walls while Li⁺ could rapidly transport along the negatively charged outer walls.^[27,58] Moreover, its negatively charged 1D structure connects the highly conductive LLYZTO, forming locally continuous Li⁺ transport pathways and numerous these local pathways combined, which fundamentally built a highway for long range Li⁺ diffusion. Impressively, the σ of PLLH-HE reached 1.06×10^{-3} S·cm⁻¹, indicating that the synergy between HE-ZIF and HNTs could further improve the electrical properties of the CSEs (Fig. 5c). In addition, the σ of the CSEs gradually increased with increasing temperature from 30 °C to 100 °C as shown in Fig. S11 (in ESI). The σ of PLLH-HE at 60 °C was 1.76×10^{-3} S·cm⁻¹ which outperformed other PVDF/LLZO-based CSEs reported so far.^[17,49] The Arrhenius plots in Fig. 5(b) show that the activation energy of PLLH-HE was 0.13 eV which was lower than that of PLL (0.17 eV), PLL-HE (0.15 eV), and PLL-HNTs (0.14 eV), indicating that it had the fastest kinetic behavior (Fig. 5c). Linear sweep voltammetry (LSV; Fig. 5d) was used to evaluate the electrochemical windows of the

CSEs. Compared with PLL-HE (1.53–5.52 V) and PLL-HNTs (1.13–5.62 V), PLLH-HE displayed a wider electrochemical window (0.89–5.71 V), implying that PLLH-HE could match high voltage cathode materials. This wider electrochemical window was attributed to the Lewis acid sites in HNTs and HE-ZIF, and the strong interactions with Vinylidene Difluoride (VDF) chains and TFSI⁻ anions, which inhibited the decomposition of the electrolyte at high potentials.^[59] The high t_{Li^+} of the CSEs facilitates the charge transport process and suppresses the growth of lithium dendrites. The t_{Li^+} of PLLH-HE in Fig. 5(e) was 0.86, which is slightly higher than that of PLL-HE and PLL-HNTs, but significantly higher than that of PLL (Fig. S12 in ESI and Fig. 5f). The high t_{Li^+} of PLLH-HE can be attributed to the rich Lewis acid sites on the LLYZTO and HE-ZIF particles, which restricted TFSI⁻ movement and facilitated Li⁺ migration.^[21,36] On the other hand, the positively charged inner walls of HNTs and sub-nanometer pores of HE-ZIF also selectively anchored negatively charged TFSI⁻ anions.^[27,36,41,47]

The cycling performance of the CSEs for lithium stripping/plating at different current densities was evaluated using Li symmetric batteries (Li//CSEs//Li). As shown in Fig. 6(a), the Li//CSEs//Li exhibited excellent cycling stability at 0.2 mA·cm⁻² and no short circuits occurred after 2000 h of cycling. The locally enlarged curves showed that in contrast to other cells, Li//PLLH-HE//Li displayed smaller polarization and a stable voltage curve (Figs. 6b and 6c). At this current density, the interfacial impedance of the Li//PLLH-HE//Li after 500 cycles was relatively low (approximately 62 Ω), which indicates that the containing HE-ZIF and HNTs fillers had superior interfacial compatibility and stability (Fig. S13 in ESI). At a current density of 0.5 mA·cm⁻² in Fig. 6(d), the polarization voltages of Li//PLL//Li, Li//PLL-HE//Li, and Li//PLL-HNTs//Li increased significantly after 300, 420, and 750 h, respectively. In contrast, Li//PLLH-HE//Li still exhibited a stable polarization voltage with almost no obvious change, even after 1200 h of cycling. In addition, the voltage curve of Li//PLLH-HE//Li remains smooth without abnormal fluctuations after long-term cycling, as shown in Figs. 6(e) and 6(f). The excellent long-term stability of Li//PLLH-HE//Li stems from the high σ , opti-



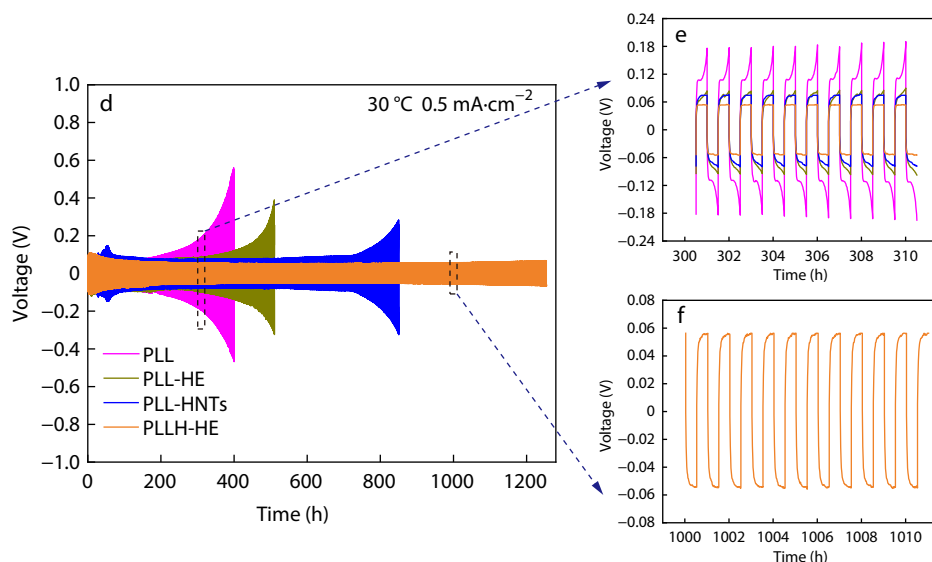


Fig. 6 (a, d) Galvanostatic cycling profiles of lithium symmetric cells with PLL, PLL-HE, PLL-HNTs and PLLH-HE at current densities of 0.2 and $0.5 \text{ mA}\cdot\text{cm}^{-2}$; (b, c, e, f) Enlarged cycling plots of Li//CSEs//Li at different periods.

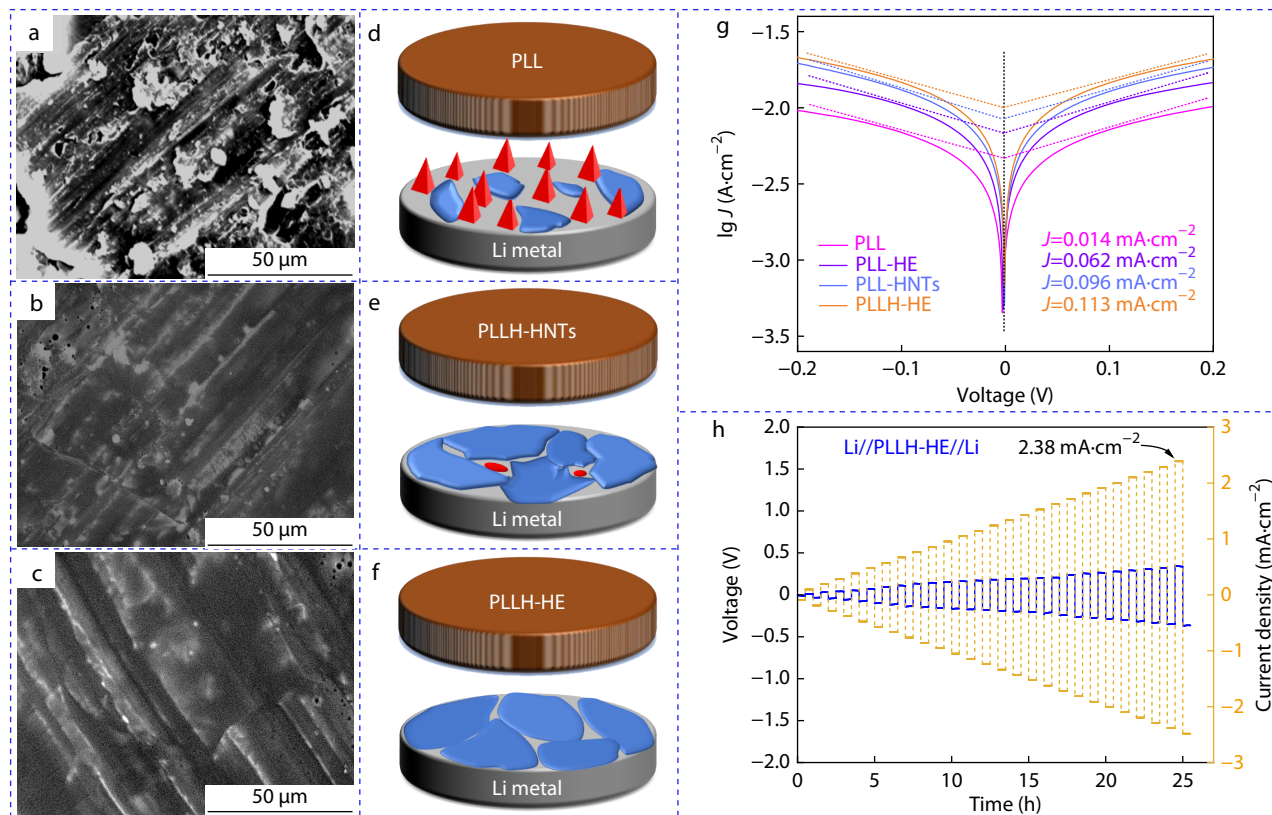


Fig. 7 (a–c) Li electrode morphology after long-term cycling for Li//PLL/Li, Li//PLL-HNTs/Li and Li//PLLH-HE/Li; (d–f) Corresponding schematics of Li dendrite behavior; (g) Exchange current density; (h) CCD of Li//PLLH-HE/Li.

mized interfacial compatibility and suppression of lithium dendrite growth as a result of the synergistic effect between HE-ZIF and HNTs.

The growth of lithium dendrites can pierce the electrolyte, thus triggering a battery short-circuit, aggravating side reactions and shortening the cycle life. By disassembling Li//CSEs//Li symmetric cells after 300 h of cycling at 0.2

$\text{mA}\cdot\text{cm}^{-2}$, the surface morphology of the Li-metal electrode was observed. For the PLL electrolyte, the Li-metal electrode presented a mossy and uneven surface (Fig. 7a), indicating the uneven growth of Li dendrites. In sharp contrast, a distinctly flat and smooth surface was observed when the PLL-HNTs and PLLH-HE electrolytes were employed (Figs. 7b and 7c). This phenomenon was attributed to the homogenous de-

position of Li metal as a result of the enhanced σ and compatible interface between Li and the PLLH-HE electrolyte. Figs. 7(d)–7(f) visually illustrate the surface morphological characteristics of the corresponding Li-metal electrode. The Tafel plots (Fig. 7g) showed that the exchange current densities of PLL-HE, PLL-HNTs, and PLLH-HE were markedly higher than those of PLL, indicating that the formation of a kinetically favorable charge transfer region at the Li anode/electrolyte interface after the introduction of HE-ZIF and HNTs.^[60,61] The critical current density (CCD) is a key indicator of the maximum current tolerance of lithium symmetric batteries, which is relevant to the capacity of fast-charging or discharging for LMBs. As seen from Fig. 7(h) and Figs. S14(a)–S14(c) (in ESI), CCD of Li//PLLH-HE/Li reached $2.38 \text{ mA}\cdot\text{cm}^{-2}$, which was

higher than that of PLL-HE ($2.0 \text{ mA}\cdot\text{cm}^{-2}$) and PLL-HNTs ($2.1 \text{ mA}\cdot\text{cm}^{-2}$), but 150% higher than that of PLL ($0.95 \text{ mA}\cdot\text{cm}^{-2}$). This result indicates that the superior ionic conductivity of PLLH-HE effectively inhibits the growth of lithium dendrites.

To verify the application potential of the CSEs, LFP//CSEs//Li LMBs were subjected to cycling performance tests at different rates within the voltage range of 2.5–4.0 V. As shown in Fig. 8(a), the initial discharge specific capacity of LFP//PLLH-HE/Li was $161.1 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C, with a Coulombic efficiency of 99.6%, which is comparable to that of liquid electrolyte batteries.^[49] After 200 cycles, the capacity of retention was up to 94.9%, which was significantly higher than those of LFP//PLL/Li (65.8%) and LFP//PLL-HE/Li (88.7%). Notably, LFP//PLL-HNTs/Li (94.3%) exhibited a similar dis-

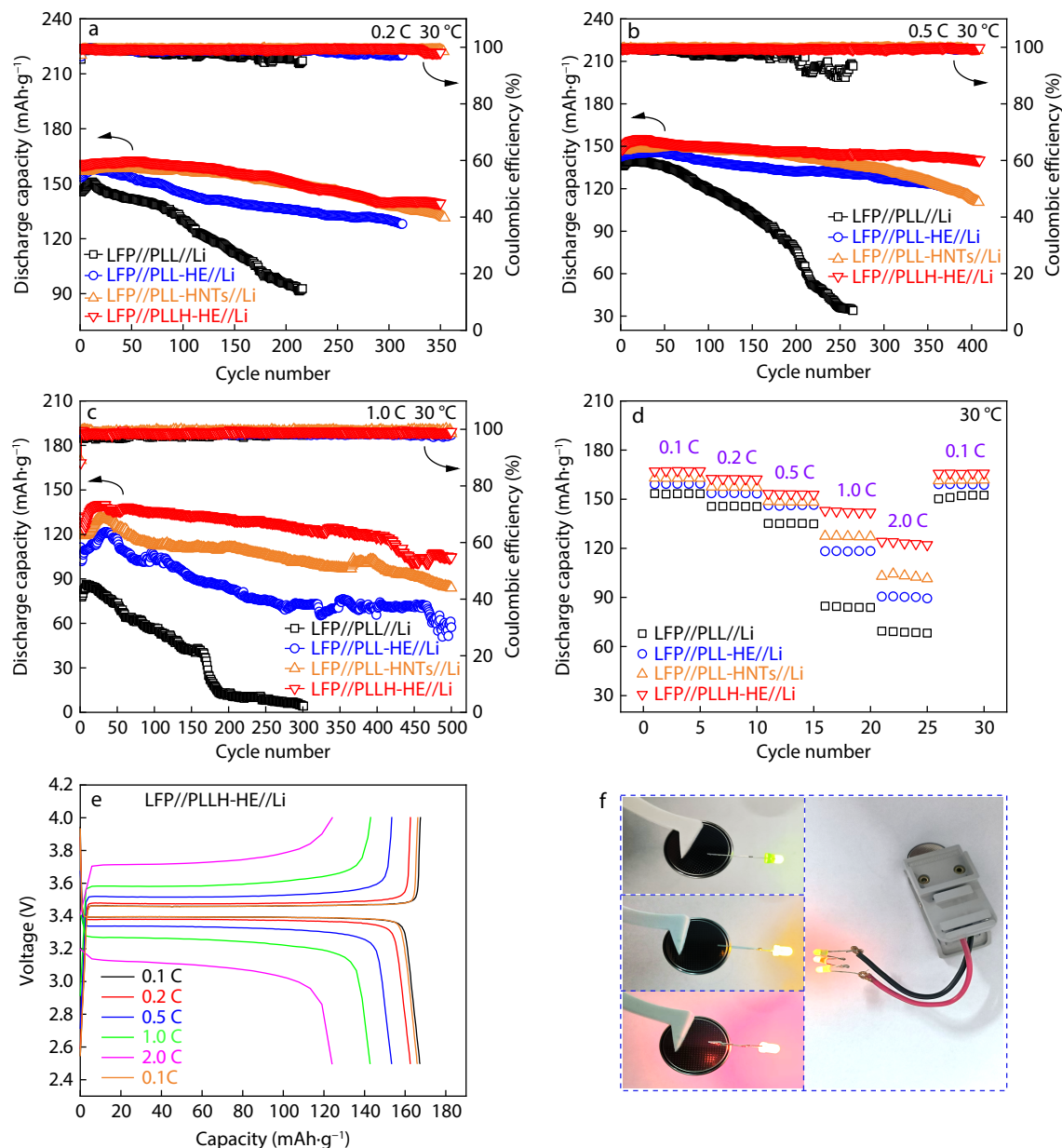


Fig. 8 (a–d) Cycle performance at 0.2, 0.5, 1.0 C and different rates performance of LFP//PLL/Li, LFP//PLL-HE/Li, LFP//PLL-HNTs/Li and LFP//PLLH-HE/Li, respectively; (e) Discharge voltage curves of LFP//PLLH-HE/Li at different rates; (f) The working state of LFP//PLLH-HE/Li cell.

charge performance similar to that of LFP//PLLH-HE//Li at this rate. Even after 350 cycles, the polarization potential of LFP//PLL-HE//Li was only slightly higher than the initial polarization potential ($\Delta \approx 0.12$ V), the discharge specific capacity remained at $139.2 \text{ mAh}\cdot\text{g}^{-1}$ with the Coulombic efficiency of 98.1% (Fig. S15a in ESI). At 0.5 C, the discharge specific capacity of LFP//PLL//Li dropped significantly after cycling, whereas LFP//PLLH-HE//Li showed excellent cycling stability throughout the entire cycling process (Fig. 8b). After 400 cycles, the discharge specific capacity of LFP//PLLH-HE//Li still reached $141 \text{ mAh}\cdot\text{g}^{-1}$, which was significantly higher than that of LFP//PLL-HNTs//Li ($113.2 \text{ mAh}\cdot\text{g}^{-1}$), indicating the favorable synergetic effect between HNT and HE-ZIF. In addition, the charge-discharge potential (charging potential of 3.58 V, discharging potential of 3.27 V) was close to the initial value (Fig. S15b in ESI), indicating that PLLH-HE had excellent electrochemical stability. As shown in Fig. 8(c), the discharge specific capacities at 1 C of the LFP//PLL//Li, LFP//PLL-HE//Li and LFP//PLL-HNTs//Li cells all faded significantly, with LFP//PLL//Li almost losing its effective discharge capability after 200 cycles. Compared with those cells, LFP//PLLH-HE//Li still exhibited ideal cycling stability and Coulombic efficiency retention capability, with a maximum discharge specific capacity of $140.2 \text{ mAh}\cdot\text{g}^{-1}$, the lowest interfacial impedance after 300 cycles (Fig. S16 in ESI), and a discharge specific capacity and Coulombic efficiency of $104.7 \text{ mAh}\cdot\text{g}^{-1}$ and 99.18%, respectively, after 500 cycles. This result further confirmed that the synergistic effect of HNTs and HE-ZIF could distinctly improve the cycling reliability of the battery at high rates. As

shown in Figs. 8(d) and 8(e), LFP//CSEs//Li all displayed stable rate performance at different rates of 0.1, 0.2, 0.5, 1.0, and 2.0 C. However, the discharge specific capacities of LFP//PLLH-HE//Li at each rate were higher than those of the other cells. As the rate increased, the charge-discharge potential of the battery increased and the discharge specific capacity decreased owing to the dynamic mismatch between the Li^+ migration rate, interfacial diffusion rate, and charge-discharge rate at high rates, and further inducing intensified concentration polarization.^[62] When the rate was switched from 2.0 C to 0.1 C, the capacity recovered to 99.2% of the initial value, reflecting excellent rate reversibility.^[17] The practicality of the LFP//PLLH-HE//Li was further verified by powering LED lights (Fig. 8f).

To further enhance the specific capacity of LMBs and make full use of the wide electrochemical window of PLLH-HE, an NCM811//CSEs//Li LMBs with a high-voltage cathode NCM811 was assembled. As shown in Fig. 9(a), the cells assembled with PLL-HE, PLL-HNTs, and PLLH-HE all exhibited good cycling stability at 0.5 C. Among them, NCM811//PLLH-HE//Li delivered the best performance. Its initial discharge specific capacity was $174.3 \text{ mAh}\cdot\text{g}^{-1}$, and the capacity still remained at $168.8 \text{ mAh}\cdot\text{g}^{-1}$ after 350 cycles with a high retention of 96.84% (Fig. S17a in ESI). In contrast, the discharge specific capacity of NCM811//PLL//Li sharply decreased after 120 cycles. The long-term cycling test at 1.0 C verified that NCM811//PLLH-HE//Li still maintained excellent stability (Fig. 9b). Its discharge specific capacity was retained at $140.1 \text{ mAh}\cdot\text{g}^{-1}$ after 600 cycles, with a Coulombic efficiency of

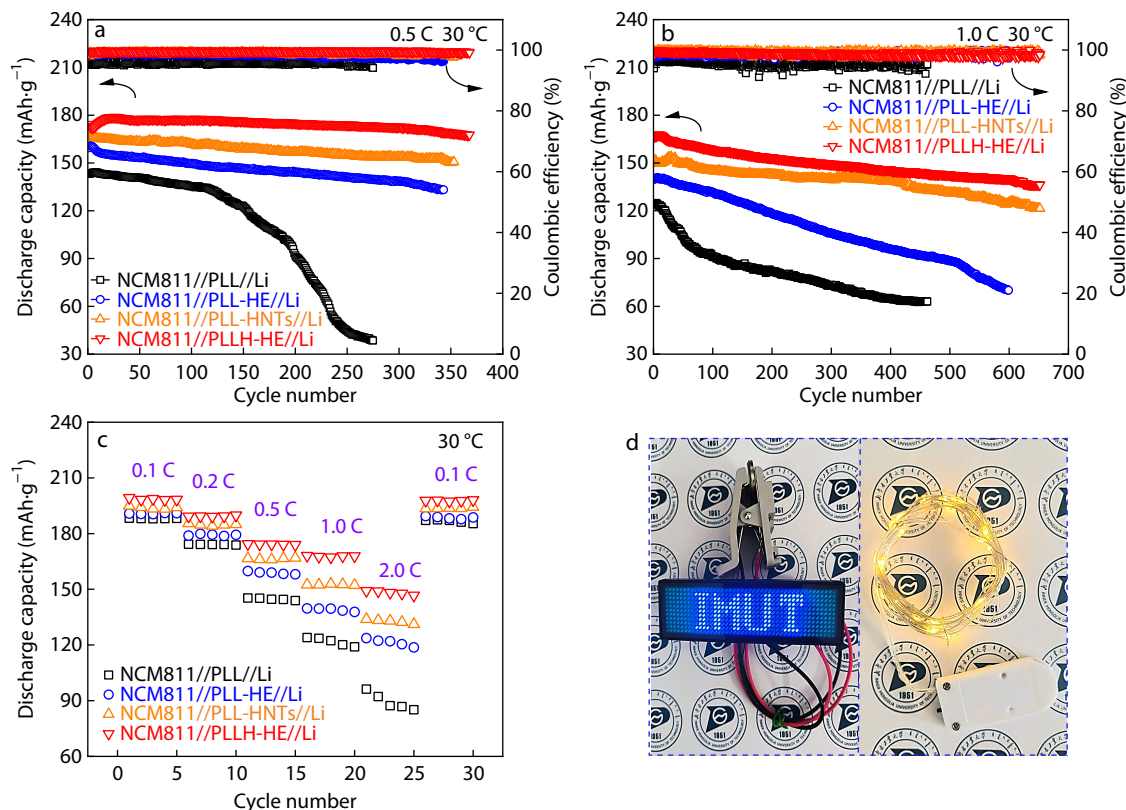


Fig. 9 (a–c) Cycle performance at 0.5 C, 1.0 C and different rates performance of NCM811//PLL//Li, NCM811//PLL-HE//Li, NCM811//PLL-HNTs//Li and NCM811//PLLH-HE//Li, respectively; (d) The working state of NCM811//PLLH-HE//Li.

98.68%. The charge-discharge curves at different cycles revealed that the polarization effect was slightly intensified with the progress of cycling (Fig. S17b in ESI). In addition, results from Fig. 9(c) and Fig. S17(c) (in ESI) demonstrated that the discharge specific capacities of NCM811//PLLH-HE//Li at 0.1, 0.2, 0.5, 1.0 and 2.0 C were 198.3, 189.4, 174.3, 168.1 and 148.2 mAh·g⁻¹, respectively. The cell still operated stably when the current rate returned to 0.1 C, indicating its good reversibility. No obvious decomposition of PLLH-HE was observed under high-rate conditions.^[48] This excellent cycling performance of NCM811//PLLH-HE//Li at various rates was attributed to the high σ of PLLH-HE and its wide electrochemical window up to 5.71 V.^[63] Single and double NCM811//PLLH-HE//Li full cells successfully powered a display screen showing the word "IMUT" and a string of LED lights (Fig. 9d).

Table S1 (in ESI) summarizes the LMBs rate capabilities of CSEs with different polymer matrices and/or LLZO, ZIF, and HNTs (either single or combined). Compared with CSEs containing a single filler (LLZO, ZIF, or HNTs) or binary fillers (LLZO/ZIF, HNTs/ZIF), the LFP or NCM811//PLLH-HE//Li exhibited a distinct advantage in discharge specific capacity. Specifically, the discharge specific capacity of the cell with LFP cathode reached 161.1 mAh·g⁻¹ at 0.2 C, which was 3.3%, 18.4% and 6.1% higher than those of the single LLZO-based electrolyte (156 mAh·g⁻¹), single HNTs-based electrolyte (136 mAh·g⁻¹), and binary LLZO/HE-ZIF-based electrolyte (151.9 mAh·g⁻¹), respectively.^[17,28,36] The capacity still reached 143.1 mAh·g⁻¹ at a high rate of 1.0 C, which was even 31.3% higher than that of the binary HNTs/ZIF-based electrolyte (105.31 mAh·g⁻¹) with LiPF₆ liquid electrolyte.^[47] For the NCM811 high-voltage cathode, the discharge specific capacity of the cell assembled with PLLH-HE electrolyte at 0.2 C was 1.47, 1.21 and 1.21 times that of the previously reported cells assembled with single LLZTNO-, HNTs- and ZIF-8-based electrolytes, respectively.^[18,28,43] These results clearly demonstrated that the synergistic effect of the HNTs and HE-ZIF in PLLH-HE not only effectively improved the σ and transfer number of CSE, but also boosted the overall electrochemical performance of LMBs, providing a general strategy for developing the high-performance solid state lithium batteries with high safety.

CONCLUSIONS

A flexible PVDF-based CSE for solid-state LMBs was prepared by innovatively incorporating 1D HNTs with potential differences between the inner and outer surfaces and a porous high-entropy ZIF. A continuous local Li⁺ transport pathway was constructed using the 1D tubular HNTs. Additionally, the differential charge characteristics on the inner and outer surfaces confined TFSI⁻ and accelerated Li⁺ migration, whereas HE-ZIF further hindered the transport of large-sized anions through the spatial steric hindrance effect provided by the porous sub-nanopores. The synergistic effect of the two fillers simultaneously improves the ionic conductivity and Li⁺ transference number. The as-prepared PLLH-HE exhibited an ionic conductivity of 1.06×10⁻³ S·cm⁻¹, a Li⁺ transference number of 0.86, and a mechanical strength of 14.63 MPa, which enabled fast ion transport and lithium dendrite suppression simultaneously. The Li

symmetric cell showed a long cycling life and a high CCD (2.38 mA·cm⁻²). The LFP//PLLH-HE//Li cell maintained a capacity of 141 mAh·g⁻¹ after 400 cycles at 0.5 C, and the NCM811//PLLH-HE//Li cell delivered a capacity of 140.1 mAh·g⁻¹ after 600 cycles at 1.0 C, showing outstanding comprehensive performance. This work lays the foundation for the development of high-energy-density solid-state LMBs with improved safety.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3738-y>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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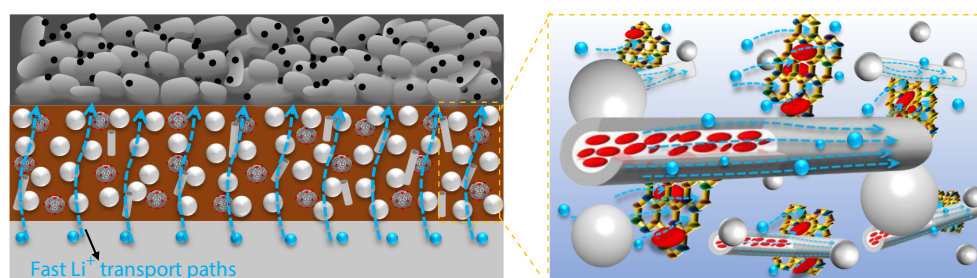
Graphical Abstract

High Ionic Conductivity and Transfer Number of Composite Solid Electrolyte for Advanced Lithium Battery by Synergetic Effect of Halloysite Nanotube and High-entropy Zeolitic Imidazolate Frameworks

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A flexible polyvinylidene fluoride (PVDF)-based composite solid electrolyte with 1D halloysite nanotubes (HNTs) and porous high-entropy zeolitic imidazolate framework (HE-ZIF) was prepared, achieving high ionic conductivity, Li^+ transference number and dendrite suppression.



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